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STRUCTURAL MODEL OF MATERIALS OBTAINED BY PRESSING AND USING BURNABLE ADDITIVES

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It is established that the structure of the solid phase of a material and the porous structure evolve in different directions: if the coordination number in the solid phase of a material increases as porosity decreases, then in a porous structure the number decreases. A universal, quite strict, structural model is proposed for high- and low-porosity ceramic materials which are obtained by pressing and using powdered, burnable, monodisperse additives.

Key words: model, structure, interparticle contact, porous ceramic, permeability, particle size, porosity, specific surface area, tortuosity of pore space, coordination number.

The stability of the properties (permeability, strength, electric and thermal conductivity) of ceramic porous and composite materials is secured by their structural type and uniformity [1 – 6]. To obtain analytic computational expressions it is helpful to use monodisperse models which take account of the fabrication technology used for porous and composite materials. The present work proposes a universal, quite strict, structural model of high- and low-porosity ceramic materials obtained by pressing (including high-temperature pressing with simultaneous sintering of the material) and with the use of powdered, burnable, monodisperse additives.

The structural and percolation characteristics of nonuniform systems depend on the coordination number of the corresponding model lattice and are related with the volume concentration V of particles of the solid disperse phase or the porosity $P = 1 - V$, which determine the average coordination numbers Z_{sol} and Z_{por} of lattices consisting of ceramic particles and pores, respectively.

For clarity we shall consider only a porous ceramic. Its parameters (porosity P, specific surface area S_0, tortuosity ξ of the porous space of the material and the average pore radius r) are determined using equations from [5]:

$$V = 1 - P = \frac{(1 - 2/Z_{sol})^2}{8 \times (1.077 - 1/Z_{sol} - Z_{sol}^{-1.16}) \times (0.5 - h/D)^3}$$

$$h = h_0 - 4h_0^2(1.5D - h_0)/(3d^2); \quad (1)$$

where $h_0[D^2 - (D^2 - d^2)^{0.5}]/2$ is the height of a spherical segment per contact;

$$S_0 = 6(1 - P)\frac{1 - Z_{sol}[h_0/D - d/D(h_0 - h)/D]}{D}; \quad (2)$$

$$\xi = \frac{2}{P[1 - (1 - 2h/D)\ln P]/\varphi + 0.2(1 - P)^2}, \quad (3)$$

$$r = 2P/(\xi^{0.5}S_0), \quad (4)$$

where h/D is the normal deformation of a particle in the zone of cylindrical contact; h is the local decrease of the particle diameter D due to contact with another particle; d is the average size of interparticle contacts; S_0 is the free surface area to volume ratio of the porous material; the coefficient φ takes account of the shape of the particles (for spherical particles $\varphi = 0.5$); and, $0.2(1 - P)^2$ is a correction for the effect of polydispersity on the resistance of the fill with a corresponding decrease of the tortuosity of the capillaries.

It is generally accepted (see, for example, [7]) that the porous structure and the structure of the solid phase possess, along with the same porosity, the same coordination numbers Z_{sol} and Z_{por} also. This is possible theoretically, but in real materials the evolution of the porous and solid-phase structures change with the porosity mainly in opposite directions, as will be shown below. Such a change of the material can be described by a universal structural model consisting of cubic and octahedral cells transforming with porosity decrease or increase into elementary semi-regular polyhedra (truncated octahedra). This makes it possible to describe quite accu-

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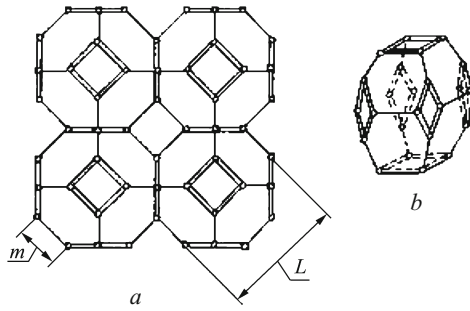
Fig. 1. Diagram of the unit cell of the structural model of mono-dipserse low-porosity materials: *a*) fragment, top view (same as side view); *b*) solid phase in a unit cell.

rately the structural evolution of the material in the entire range of the porosity P or volume concentration V of the disperse phase from 0 to 1. The semi-regular polyhedra are bounded by eight regular hexagons and six square faces (each have 36 edges and 24 vertices).

The initial structure of the powdered materials is random packing with $Z_{sol} = 7.3$ and $P = 0.37$ for smooth particles (for rough, prolate or irregularly shaped particles P can reach 0.4 or more). In the main the unit cells are octahedral (the central particles are octahedral (the central particle touches four other particles at the top and bottom) with $Z_{sol} = 8$ and $P = 0.3954$ (first structural variant) and in part cells in which the central particle touches six other particle on the side and along a particle at the top and bottom with $Z_{sol} = 8$ and $P = 0.320$ (second structural variant). Both variants are realized simultaneously in the proportion $0.3954 x_1 + 0.320(1 - x_1) = 0.37$, whence $x_1 = 0.663$, where x_1 is the fraction of the particles that form the first structural variant.

Since in a real material many cells are distorted, some contacts are broken and the coordination number decreases to $Z_{sol} = 7.3$.

The pores form an approximately simple cubic network of pores connected by rectangular through channels (see Fig. 3*a*). The coordination number of the network is $Z_{por} = 6$. In the second variant $P = 0.320$ and the number of throats in

a cavity of the unit cell $Z_{por} = 5$ (3 along the horizontal and 2 along the vertical).

The average coordination number of a porous lattice $Z_{por} = 6 \times 0.663 + 5 \times 0.337 = 5.663$.

The decrease of the porosity of ceramic materials, i.e., compaction of the powdered structure, is a result of the mutual deformation of the particles with transformation of the second structural variant into the first one and with the formation of eight primary cylindrical contacts (faces of octahedra) first and then six more secondary contacts. The rectangular through channels gradually transform into couple tetrahedral pores with $Z_{por} = 4$ (whose opposite faces are mutually perpendicular). Subsequent compaction proceeds with an increase of the contact surface area and transformation of the primary contacts into hexagonal contacts and the secondary contacts into square contacts. The result is a continuous structure consisting of elementary, semi-regular, truncated octahedra, whose incompletely formed edges comprise a capillary network with $Z_{por} = 4$. We note that the capillaries (pores) around the square contacts are wider than the other capillaries.

Such semi-regular, truncated octahedra (for $P = 0$) fill the space completely (see Fig. 1) and the average number of vertices in the faces of a polyhedron is 5.143, which corresponds to the experimental data [8].

The values of the porosity for values of Z different from the data of [2] are presented in Table 1. With the exception of the porosity with $Z = 4$ and $Z = 6$ the computational results obtained with the expression (1) agree well with the known values (for $Z = 8$ the value of the porosity lies between two known regular packings with this value of Z).

The structural evolution of the material toward increasing porosity lowers Z_{sol} to 4 and lower (and increases Z_{por} to 14). That is, the porosity of the structure changes similarly to the structure of the solid phase in a low-porosity material.

To increase porosity to $P = 0.4764$ and $Z_{sol} = Z_{por} = 6$ in the material, in which spherical ceramic particles form a simple cubic lattice with spacing equal to the average size of these particles, it is necessary to use powered burnable additives with particles of size approximately $0.97D$ (about 47 vol.%).

TABLE 1. Porosity for Different Values of Z of the Network of a Powdered System with Point Contacts ($d = 0$)

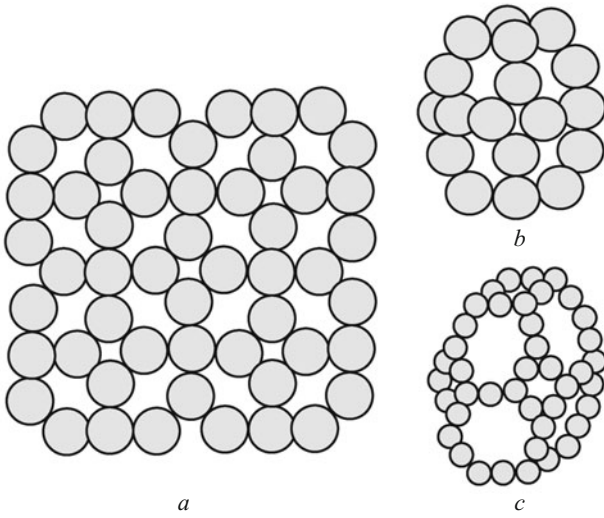| Indicator	With coordination number of the network Z_{sol}					With critical coordination number	
	4	6	8	12	14	$Z_{sol,cr} = 2.64$	$Z_{por,cr} = 1.5$
P, %:							
from Eq. (1)	0.60	0.434	0.348	0.2594	0.843	0.843	–
from [2, 9]	0.660	0.4764	0.395 0.320	0.2594	0.83	–	–
P^*, %	0.722	0.476	0.37	–	–	–	–
Z_{por}	14	6	5.66	–	4	4	14
Z_{por}/P_{cr}^*			Not determined			14/0.843	1.5/0.884

* For the proposed model.

Fig. 2. Diagram of the unit cell of the structural model of mono-disperse high-porosity materials: *a*) fragment, top view (same as side view); *b*) solid phase, forming edges in a unit cell (when the particles are located at the vertices of polyhedral); *c*) outer view of a unit cell, each edge of which is formed by three particles.

Fig. 3. Model of structural compaction: *a*) $Z = 8$; *b*) $Z = 14$; *1*) top layer of particles (odd layer); *2*) bottom layers (even).

The pores in the finished ceramic can be represented as semi-regular truncated octahedra with edge D, whose truncated vertices form square throats with edge approximately $0.75D$. The lattice cavities are interconnected by six square throats with equivalent radius $r_{th} \sim 0.26D$. The cavity in a unit cell with $Z_{sol} = 6$ is bounded by part of the surface of eight spherical particles. According to Eq. (1) the porosity of the system with $Z_{sol} = 6$ is 0.434.

To calculate the average radius of the pore throats with $4 \le Z_{sol} \le 6$ it is necessary to take account of the fact that for $Z_{sol} = 6$ $r_{th} \sim D/4$. For $Z = 6$ the average value $r_{th} = (6/4 + 8 \times 0.58)D/14 = 0.44D$. Using linear interpolation on the co-ordination number we obtain

$$r_{th} = [0.26 + 0.09(6 - Z_{sol})]D, \quad 4 \le Z_{sol} \le 6. \quad (5)$$

The subsequent transformation of the pore lattice with $Z_{por} \to 14$ into a high-porosity structure $P \to 1$ can be represented as decompaction of the powdered structure. Decompaction is accompanied by the formation of hexagonal pores. The result is a high-porosity structure consisting of pores in the form of elementary, semi-regular, truncated octahedra forming a network with coordination number $Z_{por} \le 14$, where the edges of the octahedra have a volume lattice comprised of ceramic particles with $Z_{por} = 4$.

If all particles occupy vertices of a polyhedron, then the number n of particle centers per edge of a polyhedron is 2 and the coordination number of the network $Z_{sol} = 4$ (see Fig. 2*b*).

In the model the porosity can be increased in the region $P \to 1.0$ with the average coordination number Z_{sol} decreasing correspondingly by increasing the value of n — the num-
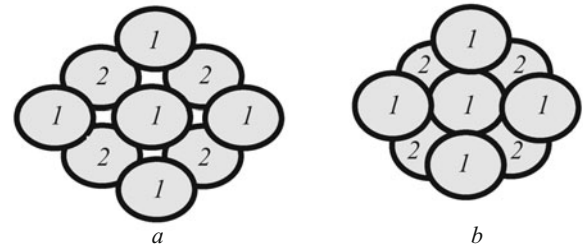
ber of interparticle contacts per cell edge — with a corresponding decrease of the particle size by the factor $(n - 1)$. For $n = 1$ all particles of the ceramic phase in a cell occupy the vertices of the cell and together comprise the volume $6\pi D^3/6$. For $n = 2$ the edges acquire thirty-six particles which belong to three cells simultaneously and comprise the volume $2\pi D^3$ of the ceramic phase in the cell.

An exterior view of a unit cell, each of which is formed by three particles, is shown in Fig. 2*c*. Since the 24 particles occupying the vertices of an elementary polyhedron belong to four cells simultaneously while the particles on the 36 faces between the vertices of an elementary polyhedron belong to only three cells simultaneously and the particle size decreases n-fold, the volume of the solid phase in the cell can be expressed as $V_{sol} = \pi D^3 (1 + 2n)]/n^3$.

The unit cell volume (see Fig. 2) is determined from the volume V_{oct} of a regular octahedron with edge $L = 3m$ ($V_{oct} = 0.4714 \times 27m^3$) minus six regular pyramids with edge $m = nD$ and volume $2^{0.5}m^3/6$. The result is the volume of a unit cell V_{cell}, equal to $V_{cell} = 11.314m^3$. Since for $n = 1$ we have $m = D - 2h$, the porosity of the system can be calculated from the expression

$$P = 1 - \pi D^3 \frac{1 + 2(n-1)}{11.34 n^3 (D - 2h)^3}. \quad (6)$$

For $n = 1$ and $h = 0$ we obtain $P = 0.722$, and the fraction of the particles of the burnable phase is $0.722/(1 - 0.722) = 2.6$. That is, the volume of the burnable phase must be 2.6 times greater than the volume of the ceramic component. According to the expression (1) $P = 0.60$. Hence, simple cubic cells as well as cells in the form of truncated octahedra are present simultaneously in the proportion $0.722x + 0.434(1 - x) = 0.60$, whence $x = 0.5/6$.

We shall determine the average coordination number Z (number of contacts per particle) as follows:

$$Z_{sol} = \frac{24 \times 4 + 36 \times 2(n-1)}{24 + 36(n-1)}. \quad (7)$$

We obtain from the expression (7) $Z_{sol} = 2.5$ for $n = 3$ and $Z_{sol} = 2.36$ for $n = 4$.

TABLE 2. Computed Parameters of the Structure of Monodisperse High-Porosity Ceramic Materials with Point Contacts ($d = 0$)

n	Z	r_{th}/D, from Eq. (8)	P, % from Eq. (6)	P, % from Eq. (1)
1	4.0	0.443	0.722	0.600
2	2.8	1.117	0.896	0.872
3	2.5	1.825	0.949	0.937
4	2.364	2.539	0.970	0.963

We shall determine the average radius of the throats from their rms value, taking account of the area $2.5981D^2$ of a hexahedron:

$$r_{th}/D = \frac{8(2.5981n^2 - 0.75\pi n - 0.25\pi) + 6(n^2/\pi - 0.5n + 0.25)}{\sqrt{14\pi}}. \quad (8)$$

The values of r_{th} for different values of n are given in Table 2.

In low-porosity materials we assume that the pores are regular tetrahedra with edge a. The volume of a tetrahedron is $0.1179a^3$. Equating the area of a triangle expressed in terms of the perimeter to its area in terms of the product of its base by its half-height we obtain the height of the triangle in the central section passing through a lateral edge and the bisector of the opposite face. We obtain an equilateral triangle with base a and included angles 54°40′. The point of intersection of the two altitude lines drawn to the opposite sides is the center of the tetrahedron. Thus, the distance of the center to a vertex of the tetrahedron is $r_{tet} = 0.5a/\sin 54°40′ = 0.6124a$.

We find the porosity of the system from the condition that the number of pores per cell is one-fourth the 24 pores (vertices), since each pore is bounded by four cells:

$$P = \frac{6 \times 0.1179a^3}{11.1137m^3} \quad (m \text{ — see Fig. 1}).$$

We shall now find the critical porosity (when the tetrahedral pores no longer overlap in the narrowest parts — on the common faces of hexagonal contacts). We take account of the fact that the area of the square faces is one-half that of the hexagonal faces. And, since the possibility of conduction is determined mainly by the hexagonal contacts (the connected pores around the square contacts do not form through porosity), the distance r_{tet} from the center to a vertex of a tetrahedron must be increased by half, the value $r_{tet} = 0.75m$ is used.

The result is the critical porosity P_{cr} at which the porous material starts to pass gas or liquid becomes gas-permeable:

$$P_{cr} = 6 \times 0.1179 \times \frac{(0.75m/0.6124)^3}{11.1137m^3} = 0.116.$$
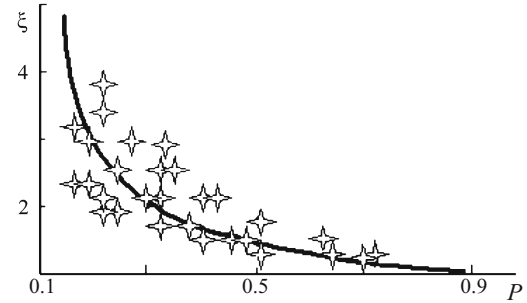
Fig. 4. Tortuosity ξ of porous space versus porosity Po: solid curve) calculation using Eq. (9); stars) experimental data from [9].

According to Tertsagi's experimental data [9] the critical porosity $P_{cr} \cong 12.5\%$, which agrees well with the value calculated using the proposed model.

It follows from the model that for $r_{tet} = m$ the square faces vanish completely (they are covered by tetrahedral pores). The result is octahedral packing with coordination number $Z = 8$. Likewise, the hexagonal faces shrink correspondingly (an edge becomes equal to $3^{0.5}a/2 = 0.866a$). Then the porosity calculated from the expression (1) with $d = 0.866 \times 0.566D$ is $P = 0.208$.

Ordinarily, the expressions used for tortuosity of the porous space of a permeable material, for example, Eq. (3), neglect the fact that at critical porosity P_{cr} the tortuosity ξ_{cr} is infinite ($\xi_{cr} = \infty$). It is useful to obtain an expression for the tortuosity ξ in the entire range of porosity taking account of the critical porosity P_{cr}:

$$\xi = \frac{0.884}{(P - P_{cr})(1 - (1 - 2h/D)\ln P)}. \quad (9)$$

In Fig. 4 the curve of ξ computed as a function of the porosity using the expression (9) is compared with experimental data from [9]. It is evident that the agreement is satisfactory.

The conductivity (for example, the dependence of the specific electric conductivity or thermal conductivity versus the porosity of a high-porosity cellular materials made from metals and ceramics with very high open porosity $(80 - 97\%)$ and permeability $(10^{-9} - 10^{-10} \text{ m}^2)$ [10] can also be analyzed using a modification of the model described above (see Fig. 1), if it is assumed that the truncated octahedra are formed by prismatic bridges of length m with triangular cross section of area $2a^2 \sin(\pi/3)$, where a is the side of a triangle.

CONCLUSIONS

It was established that the structural evolution of the solid phase of material with an increase or decrease of the porosity undergoes changes which are similar to those occurring for the porous structure, but the changes are largely op-

positely directed: if Z_{sol} in the solid phase of a material increases, then Z_{por} in the porous structure decreases.

A universal, quite strict model of the structure of high- and low-porosity ceramic materials obtained by pressing and with the use of powdered, burnable, monodisperse additives was proposed.

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